



## Reversible ionic liquids designed for facile separations

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### ABSTRACT

Reversible ionic liquids can increase the application of traditional ionic liquids, such as those based on imidazolium cations, and generate new technologies along the way. While traditional ionic liquids have gained industrial and academic attention as solvents, many applications suffer from the difficulty associated with removing high boiling point products from non-volatile liquids. Reversible ionic liquids are those which can be reversed back and forth between molecular and ionic forms enabling facile separations through large in situ property changes. Thus these novel solvents lead to truly sustainable processes. An understanding of the phase behavior of these systems provides insight into the separation capability. Here we review both one- and two-component reversible ionic liquids and their applications with an emphasis on separations.

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### 1. Introduction

Ionic liquids (ILs) are salts with melting points below 100 °C. Traditional ionic liquids, such as those based on imidazolium cations, have been considered tunable solvents because of the countless combinations of cations and anions that give rise to low melting salts, where each combination produces a separate unique property set. For this reason, their use spans a range of applications including analytical chemistry, biotechnology, electrochemistry, and organic synthesis [1–4]. However, high boiling point solutes are difficult to remove from traditional ionic liquids which have a low vapor pressure and volatility. Switchable ionic liquids expand the scope of conventional ionic liquids by including a facile, built-in separation. Thus these new “switchable” or “smart” solvents lead to highly sustainable processes.

Recently, we described two-component, reversible ionic liquid (RevIL) systems based on amidines or guanidines and alcohols and one-component, reversible ionic liquids derived from silylated amines [5–7]. These systems are pictured in Fig. 1. In each of these cases, the molecular liquids react with carbon dioxide (CO<sub>2</sub>), at 1 atm, to form ionic liquids. Operationally, the ionic liquids can simply be reversed upon heating or sparging with nitrogen to release CO<sub>2</sub>. Weiss et al. also looked at reversible amidinium salts while others looked at reactions of amines tethered onto ionic liquids or inorganic/organic hybridized amines with carbon dioxide [8–12].

Like traditional ionic liquids, the properties of the RevIL systems can be tuned by altering the structures (i.e. side groups or alcohol chain lengths). Specifically, the amidine systems encompass the reaction of 1,8-diazabicyclo-[5.4.0]-undec-7-ene (abbreviated DBU) and alcohols from methanol to decanol with CO<sub>2</sub>. The guanidine systems cover 2-butyl-1,1,3,3-tetramethylguanidine (TMBG) and alcohols ranging from methanol to dodecanol. Finally, the one-component amine systems include the ionic liquids 3-(trimethoxysilyl)-propylammonium 3-(trimethoxysilyl)-propyl carbamate (TMSAC), 3-(triethoxysilyl)-propylammonium 3-(triethoxysilyl)-propyl carbamate (TESAC), 3-(triethylsilyl)-propylammonium 3-(triethylsilyl)-propyl carbamate (TetSAC), and 3-(tripropylsilyl)-propylammonium 3-(tripropylsilyl)-propyl carbamate (TPSAC) formed from the corresponding precursors (3-aminopropyl)-trimethoxysilane (TMSA), (3-aminopropyl)-triethoxysilane (TESA), (3-aminopropyl)-triethylsilane (TetSA), and (3-aminopropyl)-tripropylsilane (TPSA).

The advantages and disadvantages of each switchable system are compared in Table 1. When contrasted with their two-

**Abbreviations:** DBU, 1,8-diazabicyclo-[5.4.0]-undec-7-ene; ILs, ionic liquids; TESAC, 3-(triethoxysilyl)-propylammonium 3-(triethoxysilyl)-propyl carbamate; TESA, (3-aminopropyl)-triethoxysilane; TetSAC, 3-(triethylsilyl)-propylammonium 3-(triethylsilyl)-propyl carbamate; TetSA, (3-aminopropyl)-triethylsilane; TMBG, 2-butyl-1,1,3,3-tetramethylguanidine; TMSAC, 3-(trimethoxysilyl)-propylammonium 3-(trimethoxysilyl)-propyl carbamate; TMSA, (3-aminopropyl)-trimethoxysilane; TPSAC, 3-(tripropylsilyl)-propylammonium 3-(tripropylsilyl)-propyl carbamate; TPSA, (3-aminopropyl)-tripropylsilane;  $\lambda_{\max}$ , Nile Red wavelength of maximum absorbance.

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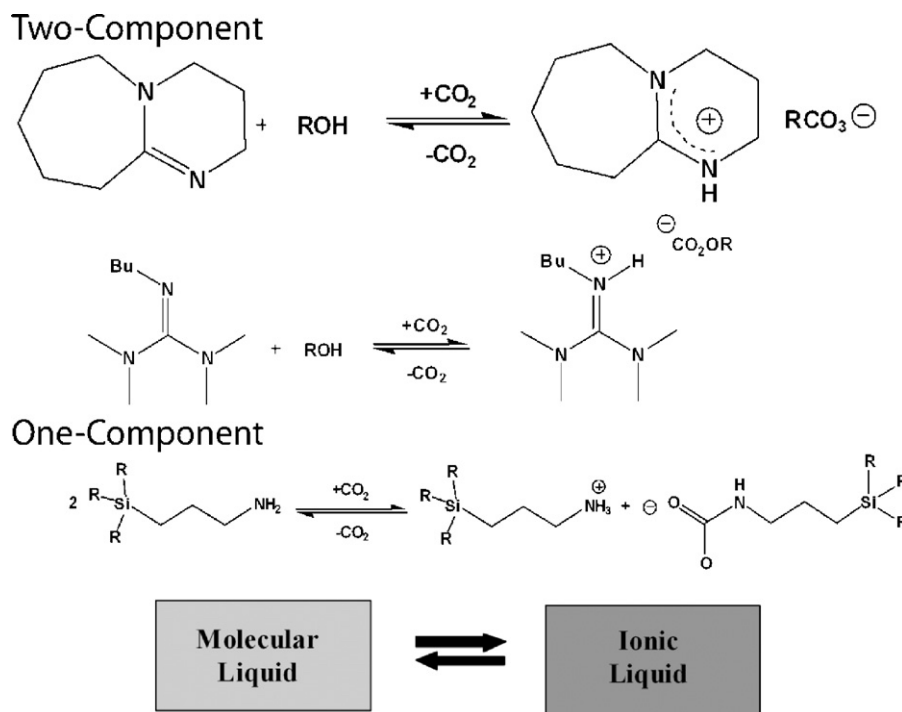


Fig. 1. Schemes for one- and two-component solvent systems.

**Table 1**

Advantages and disadvantages of reversible ionic liquid systems.

System	Advantages	Disadvantages
Two-component	Larger polarity switch between molecular and ionic liquid Lower reversal temperature Good basic solvent Lower viscosity <sup>a</sup>	Complex system Must maintain a 1:1 molar precursor ratio Low molecular weight precursors will evaporate during IL reversal
One-component	Simpler system Clean CO <sub>2</sub> stream upon IL reversal—no precursor evaporates	Higher viscosity Smaller polarity switch between molecular and ionic liquid

<sup>a</sup> Reduced viscosity may be due to an excess of one of the molecular components.

component counterparts, our one-component systems are simpler from a processing standpoint as maintaining a 1:1 molar stoichiometry (alcohol/guanidine) can be difficult. Also, upon ionic liquid reversal, the two-component systems eliminate not only CO<sub>2</sub> but also any volatile alcohols. However, the single-component RevIL produces a pure CO<sub>2</sub> stream upon reversal (discussed in more detail in the CO<sub>2</sub> capture section) eliminating the need for bothersome downstream purification. The two-component systems undergo a larger jump in polarity upon formation of the ionic liquids from the molecular precursors when compared with their one-component analogues. In addition, the two-component systems have benefits such as relatively low reversal temperatures. For example, the two-component DBU system reverses rapidly at only 50 °C [5]. In contrast, differential scanning calorimetry data for TESAC indicates the rapid loss of CO<sub>2</sub> occurs from 50 to 150 °C and for TMSAC the range is 75–175 °C [7]. The difference in properties for each type of solvent system provides a toolbox of choices that can be selected for specific applications.

Herein we include an overview of the systems' properties and examples of applications of these systems focusing on the advantages of reversible ionic liquids for efficient separations. Both of the highlighted separations are in the energy arena, where one proves selective CO<sub>2</sub> capture through solvent optimization and use of a dual physical and chemical capture mechanism and the other provides a proof of concept for the recyclable removal of contaminants from tar sands/oil shale.

## 2. Results and discussion

### 2.1. Property changes

#### 2.1.1. Viscosity

The viscosity of the reversible ionic liquids is dependent on molecular structure. Fig. 2 shows the viscosity of the one-component ionic liquids – TMSAC, TESAC, TETsAC, and TPSAC – and the two-component ionic liquid formed from TMBG and methanol. The measurements were taken using an Anton Paar rheometer, and all liquids tested were found to behave as Newtonian fluids. The

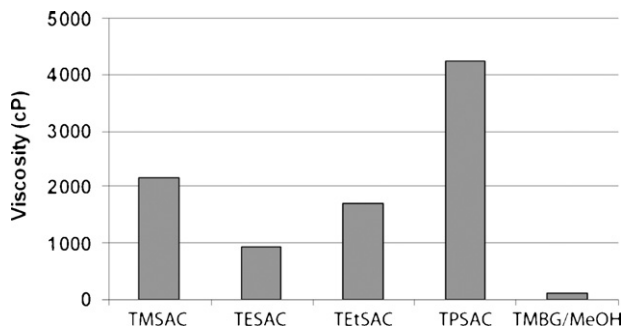


Fig. 2. Viscosity of the reversible ionic liquids.

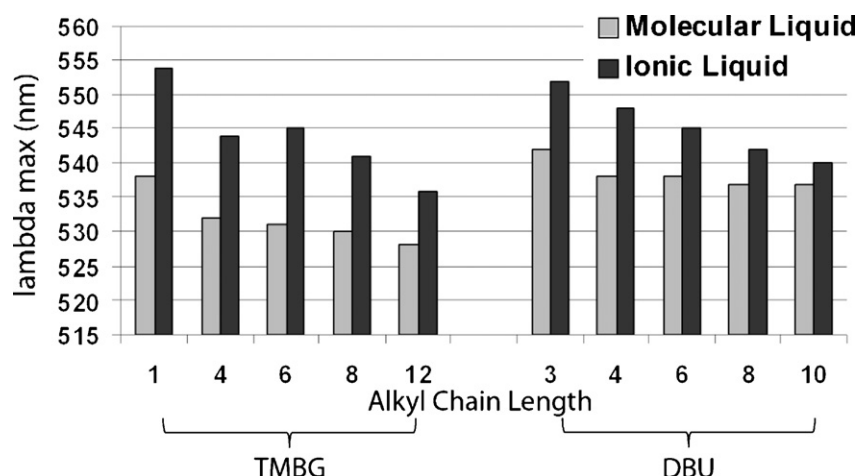


Fig. 3. Maximum absorbance of the dye, Nile Red, in the two-component reversible molecular and ionic liquids.

viscosities of all molecular liquids used here are less than 10 cP; a drastic change in viscosity is observed as the ionic liquid is formed. Although the two-component system exhibits a viscosity about one order-of-magnitude lower than the one-component systems, this may be due to an excess of one of the molecular liquids (most likely TMBG as excess methanol would have been stripped into the  $\text{CO}_2$  stream during ionic liquid formation). When comparing the one-component systems to each other it can be seen that as the side chain attached to the silicon center is increased in length, the viscosity is decreased. This is consistent with the possible disruption in the three-dimensional packing of the salt as the side chains become progressively more bulky. Also within the one-component set, the siloxylated ionic liquids are less viscous than the silylated ionic liquids of the same side chain length.

### 2.1.2. Polarity

An increase in polarity occurs upon formation of the ionic liquid from the molecular liquid, shown in Figs. 3 and 4. This polarity increase was measured using the solvatochromic dye, Nile Red, whose wavelength of maximum absorbance,  $\lambda_{\max}$ , correlates with solvent polarity and has been used for a variety of solvents including traditional ionic liquids [13,14]. The TMBG two-component systems undergo a larger jump in polarity (around 15 nm increase) than the one-component systems (around 10 nm increase) or DBU systems (around a 10 nm increase). The switch seen for the TMBG systems is akin to going from a solvent similar to chloroform ( $\lambda_{\max} = 537.6$  nm) to one similar to acetic acid ( $\lambda_{\max} = 557.2$  nm). The polarity switch seen for the DBU systems is comparable to a solvent change from *N,N*-dimethylformamide ( $\lambda_{\max} = 541.2$  nm) to one similar to methanol ( $\lambda_{\max} = 549.6$  nm). The switch seen for the one-component systems is akin to going from a solvent similar

to tetrahydrofuran ( $\lambda_{\max} = 527.6$  nm) to one similar to chloroform ( $\lambda_{\max} = 537.6$  nm). The Nile Red measurements for all systems indicate that as the overall organic content of the molecular liquids is increased, by either long silicon side chains or long chain alcohols, the jump in polarity between molecular and ionic liquid is reduced.

The change in solvent polarity can be used to enable separations as several organics are soluble in the molecular liquids but not in the ionic liquid forms. For example, octane is completely miscible with TMSA as shown in Fig. 5. Upon bubbling with  $\text{CO}_2$ , the ionic liquid TMSAC is formed. As a consequence of the polarity change, a phase split occurs: the upper phase being the octane phase and the lower phase being the ionic liquid. The switch in property was a critical asset in developing a strategy for the extraction of oil from tar sand/oil shale.

## 2.2. Selected applications

### 2.2.1. Extraction of oil from tar sands/oil shale

The removal of oil from complex feedstocks such as tar sands and oil shale is an ongoing challenge. These feedstocks are difficult to process because of their physical properties such as high viscosity and density, as well as the high content of solids. Steam has been used to extract oil from these unconventional sources, but the process is energy-intensive and produces large quantities of contaminated wastewater. Oil-miscible organic solvents can cut the viscosity of these oils enabling facile filtration, but the solvent recovery process is cumbersome and wasteful as the common method for solvent recovery, distillation, is energy-intensive and the oil's valuable low-end carbon fractions will be distilled away along with the volatile solvent. Reversible ionic liquids have potential to provide for efficient oil separation from its matrix by filtration followed by solvent recycle upon phase-splitting of oil (product phase) from the ionic liquids (solvent phase). Fig. 6 shows a proposed process flow diagram.

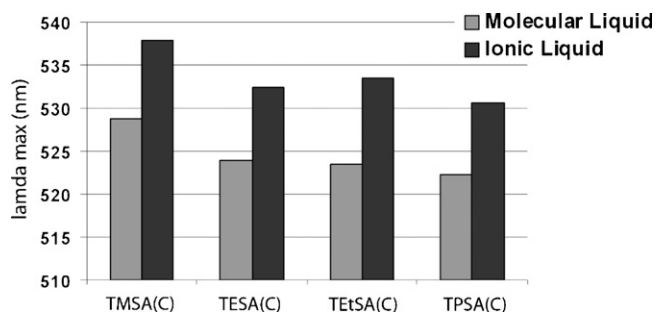


Fig. 4. Maximum absorbance of the dye, Nile Red, in the one-component reversible molecular and ionic liquids.

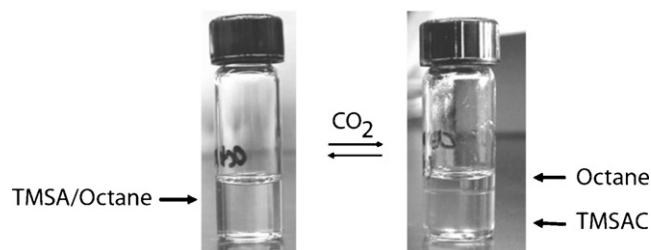


Fig. 5. Separation of octane from reversible ionic liquid, TMSAC.

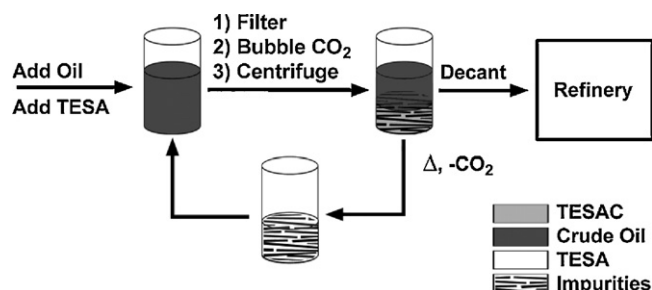


Fig. 6. Process flow diagram for the recyclable extraction of oil from contaminated feedstocks using reversible ionic liquids [7].

Blasucci et al. reported the extraction of crude oil from a tar sand/oil shale model using RevIL systems [15]. It should be reemphasized that the molecular TESA was miscible with an equal volume of oil while the ionic liquid counterpart (TESAC) phase separated from the oil. The abrupt change in the solvent's polarity allowed the authors to develop an extraction strategy and to recycle the solvent system for higher process efficiency and ultimately lower cost. Contamination of the product phase with ionic liquid was observed over the course of three cycles and remained less than 4 mol% over each cycle. It was also showed that this process can be economically beneficial when compared to the current technology [15]. We are now focusing on developing optimum solvent systems for specific feedstocks. This entails improving the mutual immiscibility of the ionic liquid and oil phase by increasing the "ionic character" of the ionic liquids. For example, as we have seen, decreasing the solvent's side chain length would increase the polarity of the solvents. However, this change is also associated with an increase in ionic liquid viscosity, which is a negative for this application. These opposing effects prove that optimization is compulsory.

### 2.2.2. Coupling reactions and separations

The switch in solvent polarity between the molecular liquids and ionic liquids allows the coupling of reactions and separations. Jessop et al. reported the polymerization of styrene in the DBU-based molecular liquid followed by removal of the product, polystyrene, by filtration from the amidinium ionic liquid [6]. The Claisen–Schmidt reaction of butanone and benzaldehyde in TMBG (which played the dual role of base catalyst and solvent) was investigated by Hart et al. [16], shown in Fig. 7. The isolation of the enone products was performed by adding octane and methanol to the reaction mixture, followed by the addition of CO<sub>2</sub>, which triggered the formation of the ionic liquid. Under these conditions an octane phase separated from the newly developed ionic liquid phase. The enone products were predominantly in the octane phase and were easily separated by decantation from TMBG.

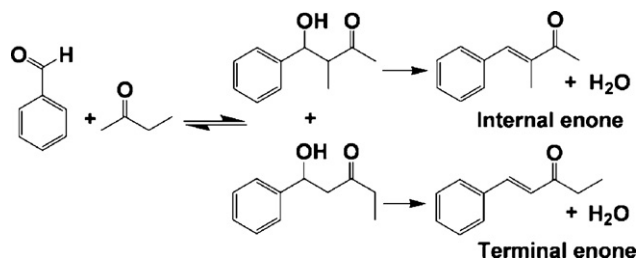


Fig. 7. Claisen–Schmidt condensation of 2-butanone and benzaldehyde.

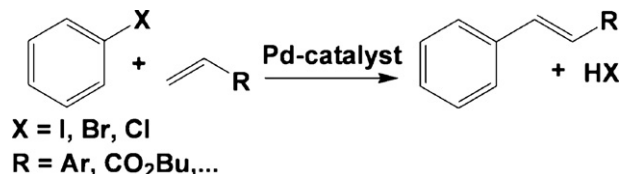


Fig. 8. General reaction scheme for Heck-type coupling reactions.

The isolated yields in enone products were 34, 32 and 34% for each cycle, with a consistent product distribution of 95% terminal enone product. Running at partial conversion was necessary in order to avoid the unwanted higher condensation products, thus allowing the facile recycle of the RevIL.

Palladium catalyzed C–C coupling reactions between an aryl halide and a substituted alkene, also known as Heck reactions, are useful chemical transformations in many synthetic processes. Heck reactions inherently cause the formation of HX (X = halide) which needs to be neutralized by a base to recover the catalyst, Fig. 8. Therefore, stoichiometric amounts of salt are formed as a by-product.

Hart et al. carried out Heck reactions in the two-component reversible ionic liquid mixture of DBU/hexanol [16]. The overall process was designed to couple the reaction, which was carried out in the ionic liquid, and a two-stage separation. First, the non-polar product was isolated from the ionic liquid. Secondly, the ionic liquid was switched to its molecular counterpart. As a result, the salt by-product precipitated out and was subsequently removed. In principle, the reversible "switch" from ionic to molecular solvent should enable the separation of product and by-product sequentially, leading to a recycling of the solvent system and the catalyst (Fig. 9).

The palladium catalyzed Heck reaction of bromobenzene and styrene was investigated (Fig. 10) for proof of principle. E-stilbene was produced as the major product. The isolated complex PdCl<sub>2</sub>(TPP)<sub>2</sub> (TPP = triphenylphosphine, PPh<sub>3</sub>) was found to give the best performance, with up to a 97% yield of E-stilbene using a catalyst loading of 2 mol%. The reaction was carried out in the ionic liquid form of the solvent, from which the nonpolar product could be isolated by extraction. Reversing the solvent to its molecular liquid state caused the salt by-product to precipitate. After separation of the salt, the solvent (containing the catalyst) was switched back to its ionic form and was used for another Heck reaction showing significant activity.<sup>1</sup>

### 2.2.3. Extraction of CO<sub>2</sub> from post-combustion flue gas streams

An enormous research challenge today is CO<sub>2</sub> capture from post-combustion flue gas. Not only are the gas streams low in CO<sub>2</sub> concentration, but the quantity of CO<sub>2</sub> that must be captured and released for sequestration is astounding. Unlike SO<sub>x</sub> and NO<sub>x</sub> emissions, there is simply too much CO<sub>2</sub> to allow for the application of a one-time use capture material. Alkanolamine based chemical absorption process have been developed and applied to the recovery of CO<sub>2</sub> from post-combustion sources. Although alkanolamine processes have proven successful on industrial scales, the inherent problem with widespread appli-

<sup>1</sup> Heck reaction recycle: The DBU/hexanol solution containing the Pd-species was treated with CO<sub>2</sub> to switch back to the ionic form, and recharged with additional preformed ionic liquid to compensate for losses from handling. Fresh substrates were added, the mixture was pressurized with 30 bar CO<sub>2</sub> and stirred at 115 °C for 3 days. After reaction, the mixture was treated as before for sequential product/salt separation and catalyst recycle. With 87% yield of E-stilbene in the first run and 55% in the second, the recovered catalyst solution displayed lower activity than fresh catalyst.

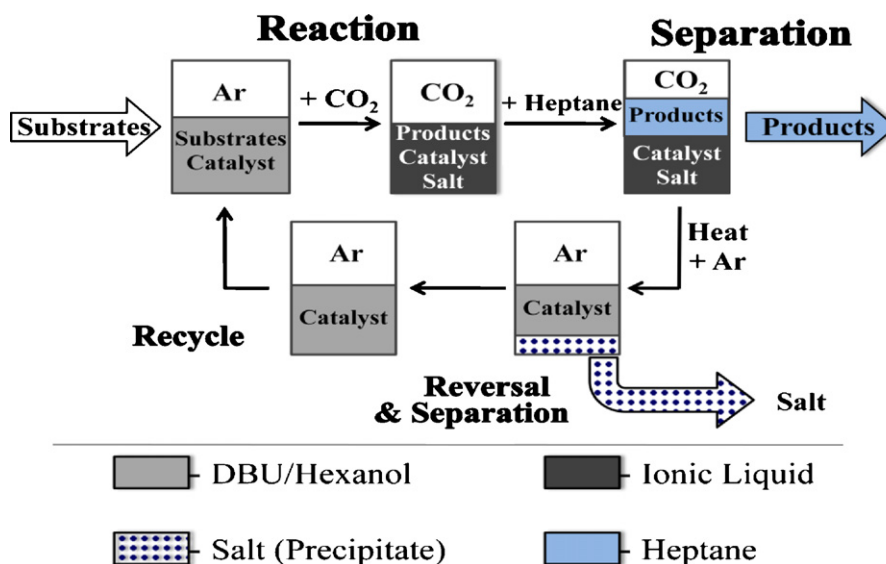


Fig. 9. General reaction/separation scheme for the Heck reaction in the reversible ionic liquid solvent system.

cation lies in the energy costs for regeneration. In an effort to offer an immediate solution to the imminent CO<sub>2</sub> regulations, it is our goal to utilize existing technology and develop an alternative solvent system to replace alkanolamines. Reversible ionic liquids have notable properties that make them ideal for the application to CO<sub>2</sub> capture from post-combustion flue gas:

1. Separation mechanism through chemical reaction yields highly selective process, critical for the dilute concentrations found in flue gas.
2. Tunable properties with respect to molecular structure allows for the design of a target compound with optimal capture and release characteristics.
3. Enhanced capacities beyond the theoretical maximum of 1 mol CO<sub>2</sub> per 2 mol molecular liquid achieved through reaction. This can be achieved by utilizing the product ionic liquid as a physical absorption solvent.

Research has been done on conventional ionic liquids for the application to CO<sub>2</sub> capture, and some candidates have shown high CO<sub>2</sub> capacities [17]. Reversible ionic liquids also exhibit high CO<sub>2</sub> loadings, but benefit from the highly selective reactive absorption mechanism resulting from the conversion of the molecular liquid to the ionic liquid. The trialkyl-substituted one-component liquids were synthesized because of water instabilities with the trialkoxy-substituted one-component liquids. Stability studies indicated the trialkyl-silyl amines were stable in wet environments for 1 month. Fig. 11 shows the physical absorption capacities of CO<sub>2</sub> in the one-

component reversible ionic liquid TPSAC at 308 and 323 K. The measurement technique was described in detail by Blasucci et al. [15]. Add to those values the capacity of CO<sub>2</sub> captured through the highly selective reaction, which is calculated to be 2.32 mol CO<sub>2</sub>/kg of TPSA, and it becomes evident that even at low pressures there is an appreciable enhancement in the chemical absorption capacity through the physical absorption of CO<sub>2</sub> into the reversible ionic liquid.

Although the two-component reversible ionic liquids can conceivably be applied to the application of CO<sub>2</sub> capture, they were ruled out as viable candidates due to the processing difficulties that arise from reversal of the ionic liquid form. Differential scanning calorimetry was used to examine the reversal of the TMBC/methanol ionic liquid and TETSA. It was seen that for the two-component system, the CO<sub>2</sub> and methanol are evolved together. Because part of the solvent is lost in the crucial regeneration step, it must be condensed and recombined in a 1:1 molar ratio with the TMBC before it can be recycled. For the case of the TETSA, the loss of CO<sub>2</sub> occurs 100 °C before the loss of solvent. To ensure industrial viability of our solvent system, and working within our guidelines to ultimately develop a replacement for alkanolamine absorbents, we conclude that the one-component reversible ionic liquids offer favorable processability over the two-component systems.

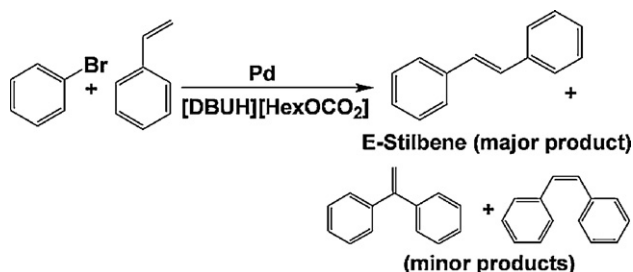


Fig. 10. Heck reaction of bromobenzene and styrene in the reversible ionic liquid [DBUH]<sup>+</sup>[HexOCO<sub>2</sub>]<sup>-</sup>.

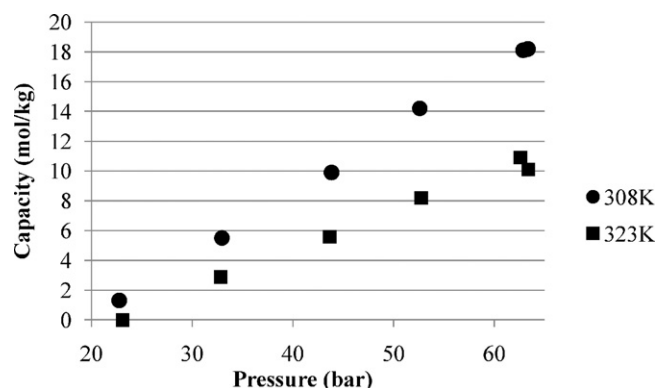


Fig. 11. Physical absorption capacities in TPSAC measured as a function of total pressure at 308 and 323 K.



### 3. Conclusions

Reversible ionic liquids can solve many of the separation problems commonly associated with traditional ionic liquids. In most respects, RevILs are analogous to traditional ionic liquids. Their physical properties such as viscosity can be altered upon structural modifications. In contrast with the traditional ionic liquids, however, RevILs can abruptly and reversibly be switched to molecular liquids. One- and two-component systems were developed for enhanced, sustainable processes. The unique switchable ability of RevIL systems allow for coupling reactions and separations into a single unit operation as demonstrated for (1) a recyclable solvent for oil recovery from oil sands, (2) the reversible coupling of Claisen–Schmidt and Heck reactions with the corresponding product purification and (3) a superior method of carbon dioxide capture from stationary point sources.

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